EFFECT OF SIZE OF THE GAP AND INITIAL STATE OF THE BRAZING FILLER ALLOY ON FORMATION OF STRUCTURE OF THE TITANIUM ALLOY BRAZED JOINTS

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Brazing filler alloys of the Ti–Zr–Ni–Cu system in both amorphous and crystalline states are widely applied in brazing of titanium and its alloys. It is reported that brazing with amorphous filler alloys creates special conditions for formation of the joints, the issue of the effect of size of the brazing gap being neglected. This issue was investigated in this study. Special samples of titanium alloy OT4 (Ti–3Al–1.5Mn) were brazed in vacuum with the fixed variable gap by using filler alloy Ti–23Cu–12Zr–12Ni in the amorphous and crystalline states to conduct comparative metallographic examinations. It was found that microstructure and chemical composition of the phases solidifying in a wide region of the seam of the joints brazed by using amorphous filler alloy Ti–23Cu–12Zr–12Ni are similar to those of the wide seams brazed with the cast filler alloy of the same composition. Primary solid solution grains and eutectic were clearly detected in structure of the seams. In the capillary gaps the seam is a diffusion zone with common base metal grains enriched with the filler alloy components, in case of brazing using both amorphous and crystalline filler alloys. Occurrence of the diffusion processes at interface between the phases is proved by the X-ray spectral analysis results. At a concentration of zirconium in the seam equal to 16.39 wt.% its concentration at a distance of approximately 100 μm deep into the base metal decreases to 1.22 wt.%, and at a distance of 150 μm zirconium is not detected at all. As shown on the basis of the results of metallographic examinations and X-ray spectrum microanalysis of the titanium joints, the decisive factor in formation of microstructure of the seams is size of the brazing gap, which determines the morphological state of the seam. 8 Ref., 5 Tables, 8 Figures.

Keywords: *titanium alloy, brazing filler alloy, gap size, joint, amorphous and crystalline state, brazed seam, microstructure*

As a rule, filler alloys in both amorphous and crystalline states are widely applied in brazing of titanium alloys. The key advantage of filler alloys with the amorphous structure is that they can be produced in the form of plastic homogeneous (in chemical composition) thin strips (30–50 μm) even from the alloys containing brittle intermetallic or eutectic phases [1]. This allows making inserted elements of any shape, strictly proportioning the amount of a filler alloy and brazing of very thin materials (e.g. heat exchangers, where thickness of a separating plate is about 0.08 mm). Owing to a high chemical homogeneity, brazing filler alloys with the amorphous structure have narrow melting temperature ranges, this ensuring good wetting of the surfaces being brazed, reducing the probability of lacks of penetration and, hence, providing a high corrosion resistance and strength of the brazed joints [2]. Such filler alloys include alloys of the Ti–Zr–Ni–Cu system, which are widely applied in brazing of titanium and its alloys [3–6].

The purpose of this study was to investigate the effect of size of the brazing gap on formation of structure of the titanium alloy seams by using filler alloys in the amorphous and crystalline states.

To produce the brazed joints, titanium pseudo α-alloy OT4 (Ti–3Al–1.5Mn) was used as a base metal. Structure of this alloy consists of the α-phase and an insignificant amount of the β-phase (1–5 %). It can be readily processed in the hot and cold states, and is used in the form of plates, bands and strips.

Brazing filler alloy Ti–23Cu–12Zr–12Ni was used in the amorphous (plastic strip 30 μm thick) and crystalline (cast ingot was crushed and used in the form of lumps) states. The filler alloy was melted in a laboratory electric-arc furnace on a water-cooled bottom plate in an atmosphere of purified argon. Each ingot was remelted not less than five times to blend its chemical composition. Titanium sponge (99.9 %), zirconium iodide (99.9 %), electrolytic nickel (99.9 %) and electrolytic copper (99.9 %) were used as source ma-

Table 1. Chemical composition of structural components of the cast filler alloy, wt.%

Investigated region	Ti	Zr	Cu	Ni
Fine grains (dark)	76.70	8.33	9.92	5.05
Phase along boundaries (light)	53.05	14.41	18.80	13.74
Eutectic	59.48	5.78	26	8.74

terials. Chemical composition of the alloys was controlled by fluorescent X-ray spectrum analysis using spectrometer VRA-30.

Before brazing, the titanium plates (2 mm thick) were mechanically cleaned and assembled in such a way that the gap between the plates had on one side a tantalum foil 150 μm wide (to fix the maximal size of the gap), and that the capillary gap formed on the opposite side between the plates. After that they were tacked with the resistance machine using the tantalum strip.

Overlap joints with a fixed variable gap (Figure 1) were brazed for metallographic examinations.

The brazing filler alloy in the amorphous state in the form of a strip was placed between the titanium alloy plates (Figure 1, *a*), and that in the cast state in the form of separate lumps was located on the plate to be brazed near the gap (Figure 1, *b*). In heating, the filler alloy with the cast structure melted and flowed into the brazing gap due to the capillary forces. Brazing of samples was performed in the vacuum furnace at a temperature of 1000 °C, the holding time being 10 min, and the degree of vacuum in the working space being $(2–5)\cdot10^{-3}$ Pa. Cooling of the samples in a temperature range of 1000–600 °C was carried out at a rate of 35–40 °C/min. Metallographic examinations were conducted by using scanning electron microscope CamScan-4 (Great Britain) fitted with energy-dispersive analyser ENERGY 200 with software INCA, and JEOL JSM 840 fitted with X-ray microanalyser of the Link system with wave spectrometer Ortec.

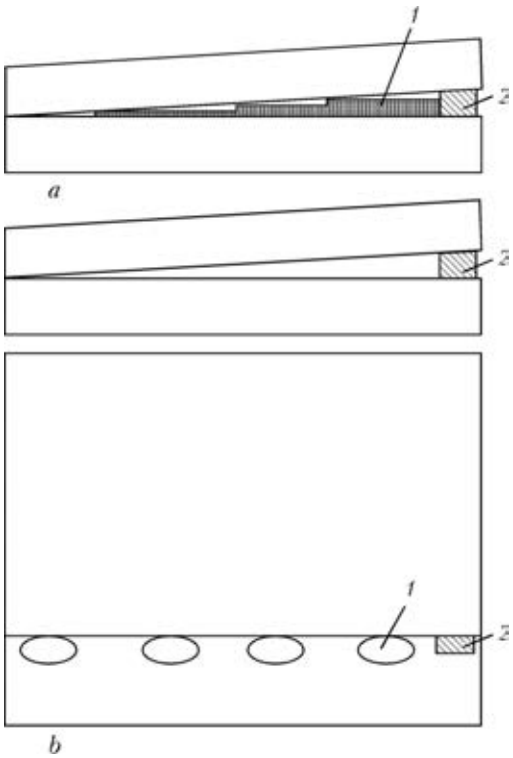

Figure 1. Schematics of samples for conducting metallographic examinations using filler alloy in the amorphous (*a*) and cast (*b*) states: *1* — filler alloy; *2* — inserted element for fixation of gap

Investigations of chemical heterogeneity of the rapidly quenched Ti–23Cu–12Zr–12Ni strip in the initial state prove the homogeneous distribution of the alloying elements in its width along the scanning line (Figure 2, *a*, *b*) [7, 8]. Structure of this alloy in the crystalline state consists of three phases (Figure 2, *c*; Table 1).

Visual examination of the brazed samples confirmed good wetting of the material being brazed, formation of smooth fillets and absence of defects. The joints brazed by using the rapidly quenched filler alloy in the amorphous state are characterised, as a rule, by formation of fillets of insignificant sizes.

At constant temperature-time parameters of the brazing process the character of solidification of the molten filler alloy in fillet regions and

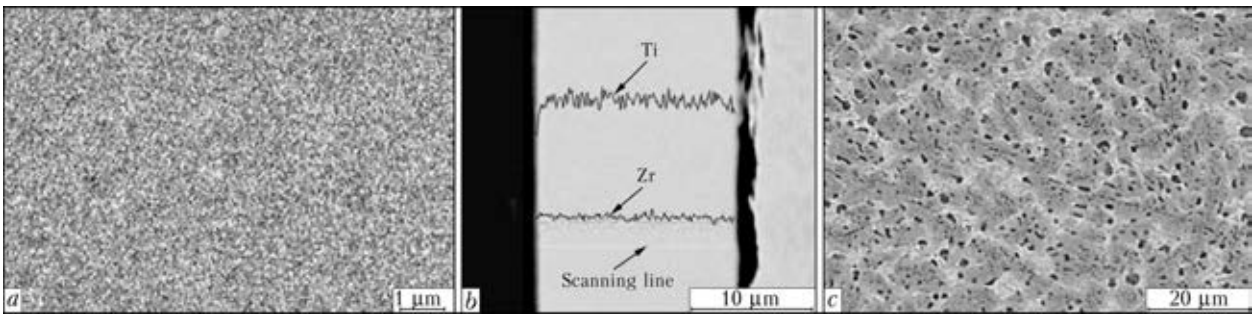

Figure 2. Microstructures of filler alloy in the amorphous (*a*) and crystalline (*c*) states, and character of distribution of alloying elements in the amorphous filler alloy (*b*)

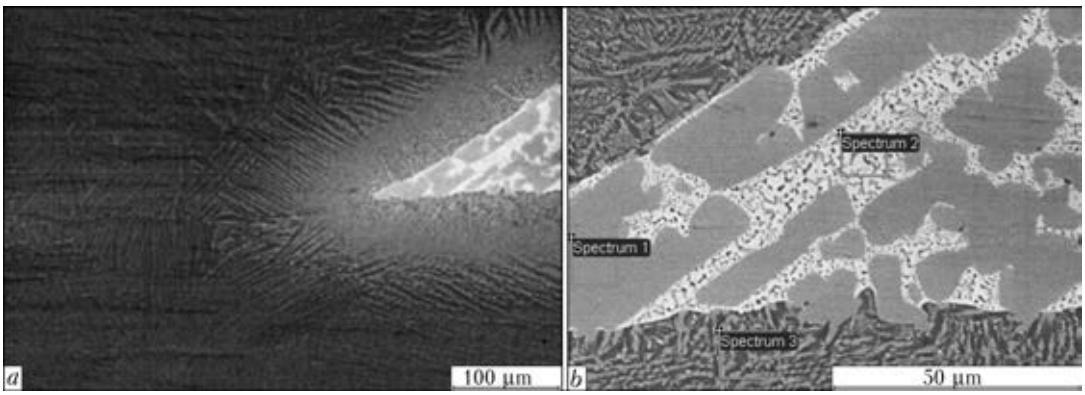

Figure 3. Microstructures of the reverse (*a*) and direct (*b*) fillets of the brazed joint made by using filler alloy with the crystalline structure

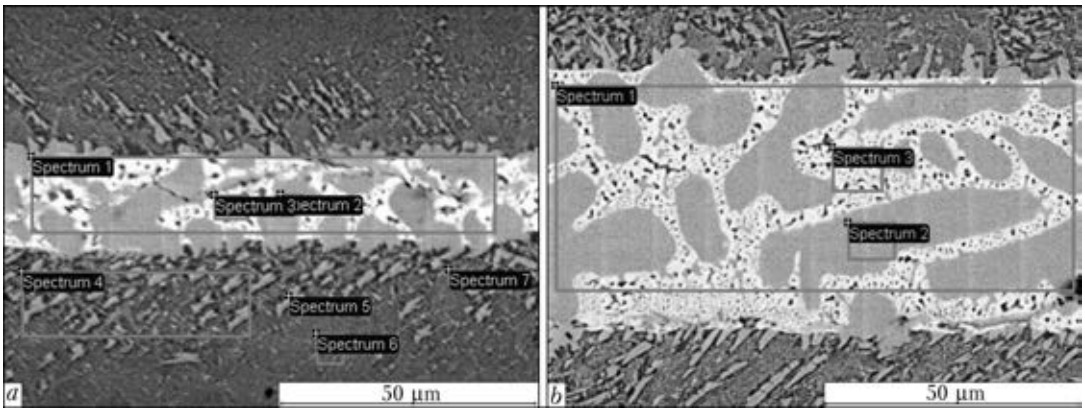

Figure 4. Microstructure of region of the brazed seam made by using filler alloy with the amorphous (*a*) and crystalline (*b*) structure

wide gaps, and morphological peculiarities of structure formation are close to each other.

For example, the full fillets, i.e. direct and reverse (Figure 3, *a*, *b*), were observed in brazing using the cast filler alloy. Metallographic examinations and investigation of chemical heterogeneity showed that the amount of structural components and their chemical composition in the fillet region and in the wide gap are practically identical (Table 2). In these regions the ratio of the amount of the molten filler alloy metal to the surface of contact with the base metal is sufficiently high, this decelerating the levelling diffusion processes. The seam metal solidifies in accordance with the main principles of solidification of cast metals and alloys.

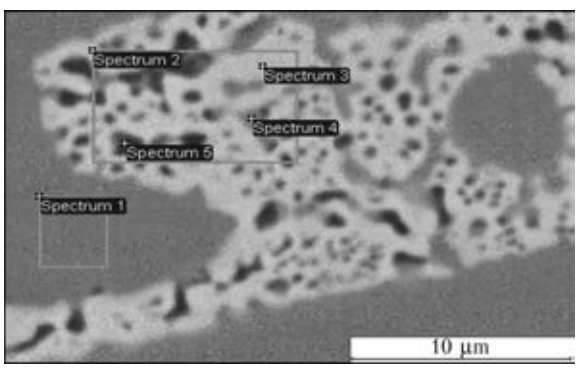

Figure 5. Microstructure of eutectic region of the brazed seam made by using filler alloy with the crystalline structure

The same structural components (Figure 4, *a*) were detected in wide-gap (40–10 μm) brazing with the rapidly quenched filler alloy in the amorphous state as in wide-gap brazing with the filler alloy in the crystalline state (Figure 4, *b*). The first to solidify was the primary phase in the form of titanium-base (54.61–54.59 wt.%) dendrites containing copper, nickel and zirconium (27.71, 7.91 and 9.49 wt.%, respectively) (spectrum 2 in Figure 4, *a*, *b*; Table 2). Then a lower-melting point phase, i.e. eutectic, with an increased zirconium content (23.12–24.40 wt.%) solidified in the dendrite spacings. A more detailed investigation of the eutectic region showed that one of the components was a complex-composition light phase enriched with zirconium (27.9 wt.%) and containing the rest of the filler alloy components (spectrum 3 in Figure 5; Table 3).

The second component of the eutectic was a dark phase, which solidified in the form of fine 0.4–1.6 μm inclusions (see spectra 4 and 5 in Figure 5; Table 3). The concentration of zirconium in this phase decreased to 19.50–20.87 wt.%.

It should be noted that the brazed seams and fillet regions contain insignificant amounts of

Table 2. Chemical heterogeneity of regions of the brazed joints, wt.%

Spectrum number	Al	Ti	Mn	Ni	Cu	Zr
Fillet region (filler alloy with crystalline structure, Figure 3, *b*)						
1	0.44	57.06	–	6.40	30.75	5.34
2	1.51	44.81	0.73	13.37	15.82	23.76
3	2	73.08	0.47	5.29	11.74	7.42
Seam (filler alloy with amorphous structure, Figure 4, *a*)						
1	0.87	50.23	–	10.43	22.90	15.58
2	0.38	54.59	–	7.91	27.71	9.41
3	1.35	46.20	0.47	12.86	14.72	24.40
4	1.81	76.08	0.55	4.47	9.93	7.17
5	0.73	60.90	–	7.01	25.82	5.54
6	1.86	77	0.38	4.56	10.16	6.04
7	1.87	75.34	1.06	5.50	6.01	10.22
Seam (filler alloy with crystalline structure, Figure 4, *b*)						
1	0.64	51.25	0.20	10.63	22.35	14.94
2	0.33	54.61	0.13	8.50	28.84	7.59
3	1.11	46.01	0.47	13.61	15.69	23.12

Table 3. Chemical heterogeneity of the eutectic region of the seam brazed by using filler alloy with the crystalline structure

Spectrum number	Al	Ti	Mn	Ni	Cu	Zr
1	0.43	54.94	0.04	8.52	28.53	7.54
2	1.06	47.85	0.58	13.62	13.53	23.36
3	1.08	39.68	0.45	16.54	14.35	27.91
4	0.60	46	0.31	13.24	20.35	19.50
5	1.15	52.39	0.38	12	13.23	20.87

aluminium and manganese, which are components of the titanium alloy being brazed. This can be explained by the mutual diffusion processes between the base material and filler alloy, which occur during brazing at interface between the phases and lead to liquation chemical heterogeneity and formation of non-equilibrium structures, as solidification of metal of the brazed seam and fillet region takes place under non-equilibrium conditions.

At constant brazing parameters (identical temperature, holding time, heating and cooling rates) a decrease in width of the brazing gap (to 4–5 μm) leads to identical changes in morphological structure of the seams brazed by using filler alloy with the amorphous (Figure 6, *a*, *c*) and crystalline (Figure 6, *b*, *d*) structure.

There were no eutectic regions in the classical meaning of this word. A flat front of solidification of the seam with formation of the two-phase structure was observed (Figure 6, *a*, *b*; Table 4). Decrease in the gap reduced the ways of diffusion

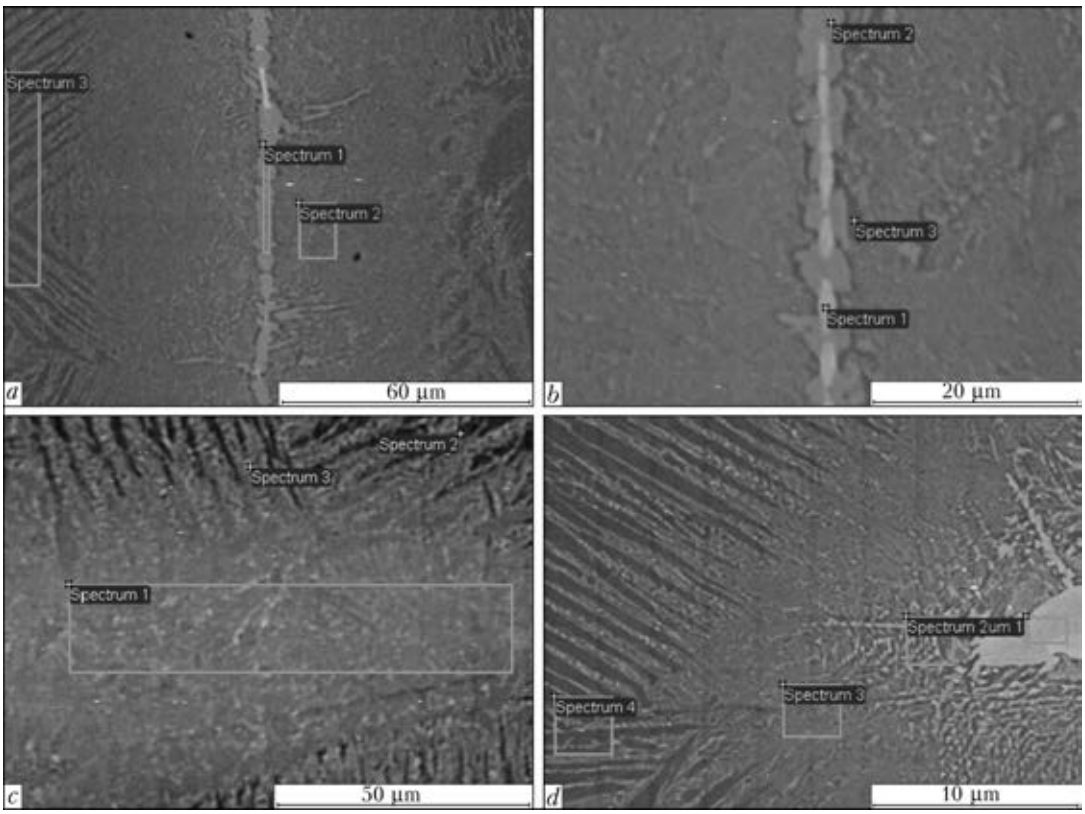

Figure 6. Microstructures of the seams made with decrease in the brazing gap by using filler alloy with the amorphous (*a*, *c*) and crystalline (*b*, *d*) structure

Table 4. Chemical heterogeneity of the seams with decrease in the brazing gap, wt.%

Spectrum number	Al	Ti	Mn	Ni	Cu	Zr
Filler alloy with amorphous structure (Figure 6, *a*)						
1	0.64	55.03	–	6.53	26.66	11.15
2	1.86	75.93	0.55	4.49	8.49	8.68
3	3.40	85.98	0.56	2.64	5.03	2.38
Filler alloy with crystalline structure (Figure 6, *b*)						
1	1.73	39.04	0.39	12.80	17.44	28.60
2	0.40	54.99	–	7.34	27.73	9.53
3	2.79	84.16	0.39	1.41	2.72	8.52
Filler alloy with amorphous structure (Figure 6, *c*)						
1	2.11	79.60	0.50	3.19	7.93	6.67
2	3.33	91.69	–	–	2.47	2.51
3	2.02	79.52	1.36	4.90	6.81	5.40
Filler alloy with crystalline structure (Figure 6, *d*)						
1	0.58	56.51	–	6.58	30.16	6.15
2	2.01	76.25	–	4.08	11.16	6.50
3	2.13	80.63	0.51	3.48	8.86	4.39
4	3	89.08	–	1.53	4.43	1.96

in the molten filler alloy, thus promoting levelling of its chemical composition in width of the seam.

Further decrease in the brazing gap when using the filler alloy with the amorphous structure led to narrowing of the seam, and the diffusion zone of common base metal grains, which is the seam, was observed in the capillary (practically zero) gap. The common base metal grains contained an increased amount of aluminium, i.e. 2.11 wt.%, and a decreased amount of components of the filler alloy (see spectrum 1 in Figure 6, *c*; Table 4). This structure was caused by the fact that the filler alloy and base metal had a common metallic base, i.e. titanium. Owing to

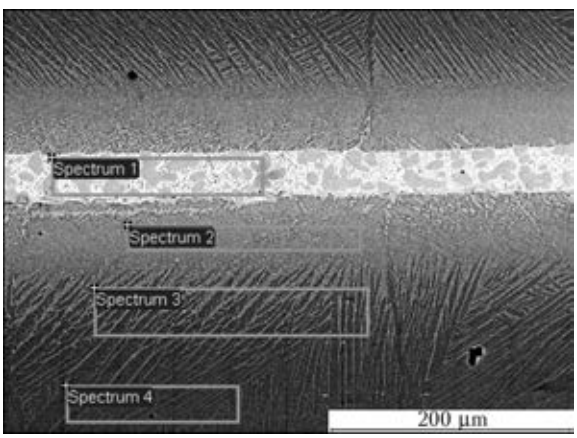

Figure 7. Microstructure of the joint brazed with the amorphous filler alloy

Table 5. Chemical heterogeneity of the joint brazed with the amorphous filler alloy, wt.%

Spectrum number	Al	Ti	Mn	Ni	Cu	Zr
1	0.68	49.61	–	12.15	21.17	16.39
2	1.92	78.40	–	4.97	9.16	5.56
3	3.22	89.10	0.74	2.60	3.13	1.22
4	3.67	95.41	0.91	–	–	–

the diffusion processes the concentration of components of the filler alloy in this zone was greatly decreased: zirconium — down to 6.67, copper — to 7.93, and nickel — to 3.19 wt.%. Metallographic examinations and X-ray spectrum microanalysis confirmed this formation of the brazed seam also in the case of using filler alloy in the crystalline state.

The cast filler alloy melted during brazing, flowed into the almost zero gap due to the capillary forces and formed the reverse fillet. There was no seam as it is in this region of the joint. Instead we saw a diffusion zone in the form of common, intergrown base metal grains based on titanium (see Figure 6, *d*) and enriched with zirconium, i.e. 4.39 wt.% (spectrum 3 in Figure 6, *d*; Table 4), like in the case of using filler alloy with the amorphous structure.

In the base metal the concentration of zirconium decreased with increase in distance from the seam. For example, in the seam the concentration of zirconium was 16.39 wt.%, whereas with distance from the seam (in the normal direction, at a distance of about 100 μm) its concentration decreased to 1.22 wt.%, and no zirconium was detected at a distance of 150 μm (spectrum 4 in Figure 7; Table 5).

The data of X-ray spectrum analysis are indicative of a high diffusion activity of zirconium and its ability to penetrate to a large depth into the titanium alloy, which is explained by an unlimited solubility of titanium and zirconium over the wide concentration ranges. The examination results indicated that the diffusion zone always contains components of the filler alloy, but in small concentrations.

As established on the basis of the results of metallographic examinations and X-ray spectrum analysis, structure of the seam metal in the brazed titanium joints made by using the given filler alloy (constant parameters of vacuum brazing) depends on the width of the brazing gap. The smaller the brazing gap, the closer is the structure of the seam to that of the base metal.

Morphological peculiarities and chemical composition of the phases solidifying in a wide

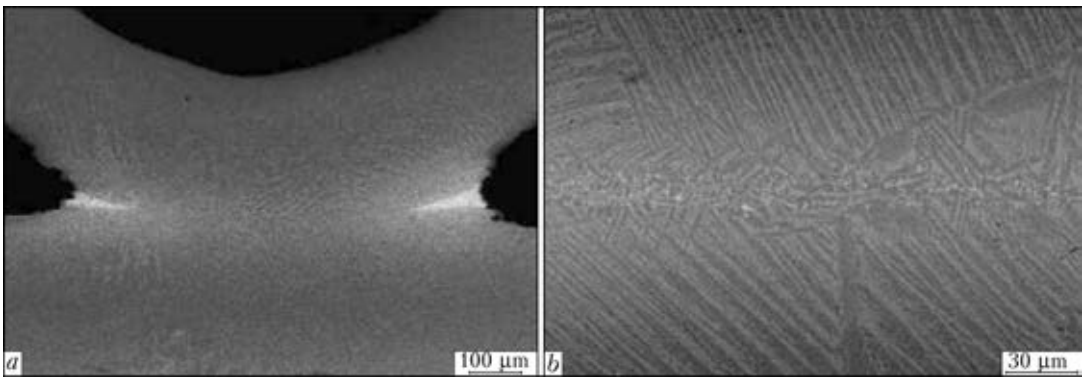

Figure 8. Microstructures of brazed fragment of the lamellar-ribbed titanium heat exchanger: *a* — general view of the joint with fillet regions; *b* — central zone of the seam

region of the seam of the joints brazed by using filler alloy Ti–23Cu–12Zr–12Ni in the amorphous state are similar to those of the wide brazed seams made by using filler alloy in the cast state. Volume solidification of metal similar to solidification of metal in an ingot is dominant in big gaps.

Brazed joints on thin-walled elements of a complex geometric shape (Figure 8, *a*, *b*) illustrating the above morphological peculiarities of structure formation are a typical example of formation of the brazed seams with a variable gap (filler alloy 30 μm thick, amorphous state). It should be noted that the use of the Ti–Zr–Ni–Cu system filler alloys in the amorphous state in the form of thin plastic strips is important for brazing of thin-walled elements of heat-exchanging titanium devices, when it is necessary to keep strictly to the brazing gap parameters and produce simultaneously (in one heating cycle) a large number of the dense brazed seams.

Therefore, it was established from the results of metallographic examinations of the titanium alloy brazed joints with a variable gap that vacuum brazing using filler alloy Ti–23Cu–12Zr–12Ni in the amorphous and crystalline states provides good formation of the brazed joints, dense sound seams and absence of any defects. The plastic thin (30–50 μm) filler alloys in the amorphous state provide the stable width of the brazing gap.

Microstructure and morphological peculiarities of the seams brazed at constant temperature-time parameters of the brazing process depend on the width of the brazing gap, rather than on the aggregate state of the filler alloy. Examinations of the brazed joints with a variable gap showed that a microstructure characteristic of the cast metal with the eutectic component forms in wide gaps and fillet regions containing a high amount of the filler alloy when using filler alloy both in the amorphous and in the crystalline state. In the capillary gaps the seam is a diffusion zone with common base metal grains enriched with the filler alloy components, which forms in brazing using filler alloy in the amorphous and crystalline states.

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